diffused to the required mutual distance, the probability of their being in the correct relative orientation is approximately 1.25%.

Thus the comparison of rates of the two reactions is consistent with the assumptions that the only significant difference between them is an outer-sphere association process of the type IV → V and that in both reactions the bulk of the electron transfer takes place over the shortest possible distances.

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Cobalt(III) Complexes of 4,7-Dimethyl-1,4,7,10-tetraazadecane. Preparations, Stereochemistry, and Reactions and the Effect of N-Methylation on Relative Isomer Stabilities

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The preparations of complexes $[Co(4,7\text{-dimetrien})X_2]^{n+}$ (4,7-dimetrien = 4,7-dimethyl-1,4,7,10-tetraazadecane; X = Cl, OH_2, NO_2; $2X = CO_3$) are described. The configurations of the racemic geometric isomers are assigned as *RR,SS*-α or *RR,SS*-β from pmr spectra and from interconversion reactions in which configurational changes at the asymmetric nitrogen donor centers are precluded by the methyl substituents. The following conversions occurring with isomerization have been observed: β-dichloro → α-dichloro; β-dichloro → α-dinitro; β-chloroaquo → α-chloroaquo; β-diaquo → α-diaquo; β-diaquo → α-dinitro; α-dichloro → β-carbonato. From the tendency for β → α isomerizations to occur and from other comparisons with the corresponding $[Co(trien)X_2]^{n+}$ complexes, it is evident that the methyl substituents enhance the stabilities of the "angular" configuration at the central amine donor atoms (stability $\alpha > \beta$) such that trans complexes with this ligand might not be obtainable.

Introduction

The chemistry of diacidocobalt(III) complexes with the flexible tetradentate ligand triethylenetetramine,[1] $[Co(trien)X_2]^{n+}$, and with homologs of trien, has attracted considerable interest and the field has been reviewed recently.[2]

Apart from the alternative trien ligand topologies,[3] alternative configurations are possible at the asymmetric secondary nitrogen donor centers giving rise to two possible configurational isomers *RR,SS* and *RS,SR*[4] for each of the β and trans topologies. Figure 1 shows all the possible isomers (one optical form of each) for complexes $[Co(trien)X_2]^{n+}$ having identical substituents X. In addition, further geometric isomers β_1 and β_2 are possible when the diacido substituents are not identical in $[Co(trien)XY]^{n+}$, and with the exception of *RS*-trans, all of these isomeric forms have now been isolated and characterized for various diacido and amino acid complexes of trien having the above formula types.[5-11] The less stable *RS*-trans configuration has however been obtained for the first time recently[12] in the complex *RS-trans*-$[Co(meso\text{-}3R,8S\text{-dimetrien})Cl_2]ClO_4$[1] where the particular dispositions of the methyl substituents on the trien backbone impose stereospecificity at the coordinated secondary nitrogen centers.

The present paper examines the isomers which may be realized for cobalt(III) complexes when the trien ligand is modified by methyl substitution at the central nitrogen atoms to create two tertiary amine functions (Figure 1).

It has been shown that the secondary N-H bonds of coordinated trien may exert considerable effect in determining the stereochemical course of various reactions.[13] Thus formation of the diaquo,[7] amino acid,[10,11] chloroammine,[14] and dinitro[15] complexes in *RS*-β[4] forms requires inversion at the "planar" secondary nitrogen center of the *RR*-β configuration. These inversions occur by N-H hydrogen exchange favored by more alkaline conditions. Similarly racemization of Δ-*RR*-β-

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(1) trien = triethylenetetramine = 1,4,7,10-tetraazadecane. It has become customary to designate alkyl-substituted derivatives according to the positions of substitution on the tetraazadecane chain for which the trivial designation trien is retained; thus 4,7-dimetrien = 4,7-dimethyl-1,4,7,10-tetraazadecane.

(2) G. R. Brubaker, D. P. Schaefer, J. H. Worrell, and J. I. Legg, *Coord. Chem. Rev.*, 7, 161 (1971).

(3) The three possible topological arrangements for coordination of trien about an octahedral metal center have usually been designated (arbitrarily) as α, β, and trans. The alternative nomenclature symmetrical cis and unsymmetrical cis for the α and β topologies in *cis*-diacido complexes has been suggested by J. H. Worrell and D. H. Busch, *Inorg. Chem.*, 8, 1563 (1969).

(4) The *R* or *S* specifications refer to the absolute configurations at asymmetric carbon atoms or at the secondary nitrogen centers of the coordinated trien ligand, according to the sequence rules of R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 5, 385 (1966). For β complexes the configuration at the normal trigonal nitrogen ("angular" nitrogen) is designated before the nitrogen center bridging the two coplanar chelate rings (the "planar" nitrogen). Δ and Λ refer to the absolute chelate configurations about the metal atom as defined in *Inorg. Chem.*, 9, 1 (1970).

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(13) G. H. Searle and A. M. Sargeson, *Inorg. Chem.*, 12, 1014 (1973).

(14) M. Dwyer, unpublished work.

(15) G. H. Searle and F. R. Keene, unpublished work.

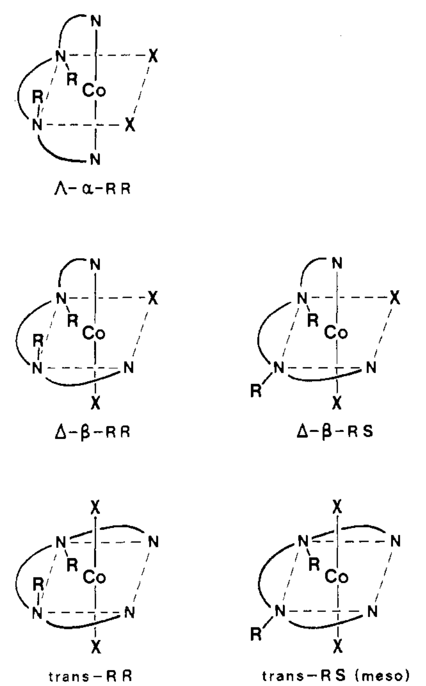

Figure 1. Geometric isomers and internal diastereoisomers of $[Co(trien)X_2]^{n+}$ (R = H) or $[Co(4,7\text{-dimetrien})X_2]^{n+}$ ($R = CH_3$).

$[Co(trien)(OH_2)_2]^{3+}$ requires inversion at this "planar" nitrogen center, although the inversion in this instance occurs in the *RR-trans*-diaquo isomer formed by initial isomerization.[13]

Clearly, the reactions of trien complexes in all conditions except aqueous acid can be complicated. In investigations of the mechanism of the hydrolysis reaction

$$\Lambda\text{-}RR\text{-}\alpha\text{-}[Co(trien)Cl_2]^+ \rightarrow \Delta\text{-}RR\text{-}\beta\text{-}[Co(trien)(OH)_2]^+$$

we encountered some difficulties due to concomitant inversion at the "planar" nitrogen center and three products were obtained which we believe to be the Λ-*RR*-α (with retention), Δ-*RR*-β (from ligand topological change only, Figure 2), and Δ-*RS*-β (ligand topological change and nitrogen inversion). To clarify these studies we required a system where the complications imposed by such nitrogen center inversions are avoided, and methyl substitution on the secondary nitrogen atoms of the parent trien provides a means of fixing the stereochemistry at these centers.

We accordingly synthesized 4,7-dimethyl-1,4,7,10-tetraazadecane,[16] hereafter abbreviated 4,7-dimetrien,[1] and the present article reports the preparations of some diacidocobalt(III) complexes in racemic forms with this ligand and the assignments of their isomeric configurations as *RR,SS*-α or *RR,SS*-β. No *RS,SR*-β isomers nor any *trans*-diacido compounds could be obtained. Interconversion reactions between these α and *RR,SS*-β complexes have been examined, and in the course of this work several isomerization reactions β → α have been observed for the first time and these should occur with concomitant configurational inversion Δ → Λ (Figure 2). Our results of more detailed investigations on some inversion reactions, employing optically active complexes, will be reported in subsequent articles.

Experimental Section

Instrumentation. Visible absorption spectra were measured on a Cary 14 spectrophotometer, and the infrared spectra in KBr disks (1.2 mg in 300 mg) were measured on a Perkin-Elmer 125 grating spectrophotometer. The pmr spectra were recorded on a Varian A-60A spectrometer (usually in D_2O or D_2SO_4 solutions using sodium trimethylsilylpropanesulfonate as internal reference), except that the diaquo spectra in $DClO_4$ (Figure 6) were recorded on a Jeol HA-100 spectrometer. The rate of aquation of α-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ in $HClO_4$ solution was measured spectrophotometrically at 350, 400, 560, and 650 nm using Perkin-Elmer 402 and Cary 16K spectrophotometers.

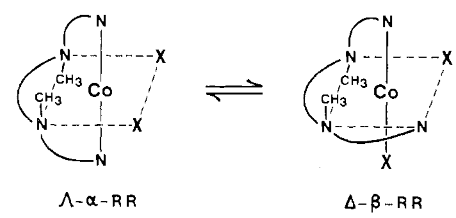

Figure 2. Possible α ⇌ β topological change, with Λ ⇌ Δ configurational inversion and preservation of the nitrogen configurations *RR*.

4,7-Dimethyl-1,4,7,10-tetraazadecane Tetrahydrochloride. The ligand was synthesized as the tetrahydrochloride salt as described previously.[16]

α-Dinitro(4,7-dimethyl-1,4,7,10-tetraazadecane)cobalt(III) Perchlorate. 4,7-dimetrien·4HCl (6.40 g, 0.02 mol) in water (60 ml) was partially neutralized by the addition of $LiOH \cdot H_2O$ (2.52 g, 0.06 mol), and $CoCl_2 \cdot 6H_2O$ (4.76 g, 0.02 mol) was dissolved in the solution with slight warming. This solution was added to a flask containing $NaNO_2$ (2.90 g) and powdered charcoal (0.5 g), and after aeration for 24 hr (with some further water added periodically) the charcoal was filtered from the yellow-brown solution and solid $LiClO_4$ (4.2 g) was added in portions. The product commenced to separate immediately as fine yellow needles, and after 2 days at 6° these were filtered off and washed with ice-cold $LiClO_4$ solution, ethanol, and ether and dried at 60°; yield 6.70 g, 79%. This product was analytically pure (Table I) and no further clean product could be obtained on evaporation. Chromatography (on SP-Sephadex C-25 and Dowex 50W-X2 ion-exchange resins, and on paper[6]) of both the isolated product and the mother liquor gave only a single yellow dinitro band.

α-Dichloro(4,7-dimethyl-1,4,7,10-tetraazadecane)cobalt(III) Perchlorate. α-$[Co(4,7\text{-dimetrien})(NO_2)_2]ClO_4$ (5.00 g) was covered with concentrated HCl in an evaporating dish, and the solution was evaporated almost to dryness over a steam bath with occasional stirring. Further HCl was added, and the process was repeated to effect the complete conversion to the purple dichloro complex. At near dryness, ethanol was added and the mixture was warmed with stirring to extract some blue cobalt(II) material into solution. The solution was decanted off, and four further extractions were carried out until the ethanol was only pale purple. The large deep purple crystals of α-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ were finally filtered off, washed with ethanol and ether, and air-dried; yield 4.36 g, 92%. See Table I for analysis.

The analogous reaction starting with α-$[Co(4,7\text{-dimetrien})(NO_2)_2]Cl \cdot 0.5H_2O$ gave α-$[Co(4,7\text{-dimetrien})Cl_2]Cl \cdot 2H_2O$, and greater reduction was evident than for the perchlorate preparation; yield 83%. See Table I for analysis.

Isolation of α-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ from the usual aerial oxidation synthesis procedure was not successful due to substantial reduction,[6,17] and the tendency to reduction appears to be enhanced with the present tertiary amine system.

α-Carbonato(4,7-dimethyl-1,4,7,10-tetraazadecane)cobalt(III) Perchlorate. Isomerically pure α-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ (2.02 g, 0.005 mol) was dissolved in 0.01 *M* $HClO_4$ (500 ml at 50°) and the solution was maintained at 50° for 1 hr, although this aquation time is not critical up to about 2 hr. The resulting violet solution of α-$[Co(4,7\text{-dimetrien})Cl(OH_2)]^{2+}$ was treated while warm with excess $NaHCO_3$ (3.0 g), and after cooling to room temperature the α-carbonato complex was absorbed on a short column of Dowex 50W-X2 cation-exchange resin, 200–400 mesh, Na^+ form. After all chloride and excess bicarbonate had been washed from the column with water, the complex was eluted from the resin with 0.5 *M* $NaClO_4$ solution. Under these conditions small amounts of dinitro (remaining in the starting dichloro) and diaquo complexes were retained on the resin. The eluent was concentrated in a rotary evaporator to a sludge from which the $NaClO_4$ was extracted with hot ethanol. The finely crystalline α-$[Co(4,7\text{-dimetrien})CO_3]ClO_4$ was finally filtered off from the ethanol solution, washed with ethanol and methanol, and

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(16) G. H. Searle, M. Petkovic, and F. R. Keene, *Aust. J. Chem.*, **25**, 2045 (1972).

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Table I. Analytical Data

Complex (L = 4,7-dimetrien = $C_8H_{22}N_4$)	% C		% H		% N		% Cl	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
α-$[CoLCl_2]ClO_4$	23.8	23.8	5.5	5.6	13.9	13.8	26.4	26.3
β-$[CoLCl_2]ClO_4$	23.8	23.5	5.5	5.5	13.9	13.8	26.4	26.1
α-$[CoLCl_2]Cl\cdot 2H_2O$	25.6	25.9	7.0	6.9	14.9	15.0	28.3	28.5
β-$[CoLCl_2]Cl\cdot H_2O$	26.9	26.5	6.7	6.6	15.7	15.5	29.7	29.8
α-$[CoLCO_3]ClO_4$	27.5	27.4	5.6	5.7	14.3	14.4	9.0	9.0
β-$[CoLCO_3]ClO_4\cdot H_2O$	26.3	26.4	5.9	6.2	13.6	13.6	8.6	8.9
α-$[CoLCO_3]Cl$	32.9	32.7	6.7	6.7	17.0	17.0	10.8	10.6
β-$[CoLCO_3]Cl\cdot 2H_2O$	29.6	29.3	7.2	7.0	15.4	15.2	9.7	9.8
α-$[CoL(NO_2)_2]ClO_4$	22.6	22.8	5.2	5.2	19.8	19.9	8.4	8.5
α-$[CoL(NO_2)_2]Cl\cdot 0.5H_2O$	26.0	25.9	6.3	6.3	22.7	22.7	9.6	9.6

dried at 60°. The pmr spectrum confirmed that this crude product was isomerically pure α. The compound was recrystallized from the minimum volume of water at 80° (7 ml) by adding ethanol (50 ml) in portions as the product crystallized. The carmine red crystals were filtered off and treated as above; yield 1.72 g, 88%. See Table I for analysis.

Conversion of α-$[Co(4,7\text{-dimetrien})CO_3]ClO_4$ to α-$[Co(4,7\text{-dimetrien})(NO_2)_2]ClO_4$. α-$[Co(4,7\text{-dimetrien})CO_3]ClO_4$ (0.393 g, 0.001 mol) was treated with excess 6 *M* $HClO_4$ (0.8 ml). Reaction occurred in the cold, but the solution was gently warmed over a steam bath (2 min) to ensure that conversion to the violet α-diaquo complex was complete. Water was added (40 ml), and then $NaNO_2$ (0.4 g) and $LiClO_4$ (0.2 g) were dissolved in the solution giving pH ~4. The now red-brown solution turned yellow over several hours, and the product began to separate out. The solution was evaporated in a current of air to a small volume (5 ml); then ethanol was added (30 ml) and the solution was left in a refrigerator overnight. The brown-yellow crystals were filtered off, washed with ice-cold $LiClO_4$ solution, ethanol, and ether, and dried at 60°; yield 0.407 g, 96%. *Anal.* Found: C, 22.5; H, 5.3; N, 19.8; Cl, 8.2. The pmr spectrum was identical with that of the α-dinitro product obtained from the aerial oxidation synthesis.

β-Carbonato(4,7-dimethyl-1,4,7,10-tetraazadecane)cobalt(III) Perchlorate Monohydrate. To a stirred ice-cold aqueous slurry of freshly prepared $Na_3[Co(CO_3)_3]\cdot 3H_2O$[18] (14.5 g in 70 ml) a solution of 4,7-dimetrien·4HCl (12.8 g in 50 ml, 0.04 mol) was added gradually. The deep red solution was then stirred and heated in a warm water bath to complete the reaction (10 min), and the hot solution was filtered. A filtered solution of excess $LiClO_4$ (6.5 g) was added and the solution was concentrated in a rotary evaporator to incipient crystallization. Some ethanol was added and the solution was left in a refrigerator to crystallize. The violet-red needles of β-$[Co(4,7\text{-dimetrien})CO_3]ClO_4\cdot H_2O$ were filtered off, washed with a little ice-cold $LiClO_4$ solution, ethanol, and ether, and air-dried. A second fraction was obtained by further evaporating the filtrate, adding ethanol, and cooling; total yield 12.7 g, 77%. The product was fractionally recrystallized from hot water (120 ml at 95°) by cooling and evaporation and then by adding some $LiClO_4$ and ethanol to obtain the later fractions (87% recovery). All fractions had identical pmr spectra. See Table I for analysis.

β-Dichloro(4,7-dimethyl-1,4,7,10-tetraazadecane)cobalt(III) Perchlorate. Hydrogen chloride was introduced through a sintered-glass diffuser into a stirred suspension of β-$[Co(4,7\text{-dimetrien})CO_3]ClO_4\cdot H_2O$ (2.00 g) in ethanol (40 ml) in a test tube cooled in an ice bath. The gas bubbling was continued only until the carbonato complex had dissolved to form a deep purple solution of the dichloro complex (1.5 min). $LiClO_4$ (0.5 g) was dissolved in the solution, and after filtering, the solution was evaporated to a small volume (by a current of cold air to remove much of the HCl), from which the product gradually crystallized. The violet-purple product was washed with ethanol by decantation until the solution remained essentially clear and was finally filtered off, washed with ethanol and ether, and dried in a vacuum desiccator; yield 1.83 g, 93%. See Table I for analysis. The dichloro complex tends to undergo reduction in the presence of HCl, but this is minimal under the above conditions. The pmr spectrum (D_2SO_4–D_2O) indicated a trace only of the α isomer (<3%).

In the analogous reaction starting with β-$[Co(4,7\text{-dimetrien})CO_3]Cl\cdot 2H_2O$ considerably more reduction occurred, and the β-$[Co(4,7\text{-dimetrien})Cl_2]Cl\cdot H_2O$ product isolated in low yield contained ~20% of α isomer. See Table I for analysis.

α- and β-Diaquo(4,7-dimethyl-1,4,7,10-tetraazadecane)cobalt(III) Perchlorates. Samples of the respective carbonato perchlorates were each treated with a small volume of 6 *M* $HClO_4$, and the solutions were warmed gently over a steam bath to complete the hydrolysis to the diaquo products. The more reactive α-carbonato effervesced on the addition of the acid, but the β isomer required warming to initiate hydrolysis.[19] After standing in a vacuum desiccator, crystals of the diaquo perchlorates had deposited after several days (α, violet; β, deep carmine) from which the solutions were removed through a small filter tube. Despite various treatments (pumping under high vacuum or washing with ether by decantation and drying in a vacuum desiccator[6]) the crystalline products could not be obtained analytically pure, and they were very hygroscopic. Spectra of the diaquo complexes were recorded on the solutions obtained by treating samples of the carbonato perchlorates with $HClO_4$ (6 *M*, then diluted to 1 *M*, electronic spectra) or 2 *M* $DClO_4$–D_2O (pmr spectra).

Attempted Preparation of β-$[Co(4,7\text{-dimetrien})(NO_2)_2]ClO_4$ and the Isomerization β → α. Method A. β-$[Co(4,7\text{-dimetrien})CO_3]ClO_4\cdot H_2O$ (0.411 g, 0.001 mol) was treated with excess 6 *M* $HClO_4$ (0.8 ml), and the solution was warmed briefly over a steam bath to effect the conversion to the carmine β-diaquo complex. The solution was diluted (10 ml) and $NaNO_2$ was added (0.4 g). After 2 days $LiClO_4$ was added (0.2 g), the solution was evaporated to a small volume (2 ml), and then excess ethanol was added (80 ml). After the mixture stood at 6°, the brown-yellow product was filtered off, washed with ethanol and ether, and air-dried; yield 0.362 g, 84%. *Anal.* Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]ClO_4$: C, 22.6; H, 5.2; N, 19.8; Cl, 8.4. Found: C, 22.6; H, 5.3; N, 20.1; Cl, 8.4. The visible, infrared, and pmr spectra and X-ray powder photograph were identical with those of the α-dinitro perchlorate.

Method B. To the β-diaquo solution prepared as in method A, a small volume of water was added (2 ml), followed by $LiClO_4$ (0.2 g) and $NaNO_2$ (0.4 g). After 1 min the solution was cooled in an ice bath and ethanol was added (12 ml). The main fraction 1 (0.26 g, orange-red) was filtered off after 15 min, washed with ethanol and ether, and air-dried. Two smaller fractions (fraction 2, yellow-orange; fraction 3, yellow) were subsequently obtained after adding more ethanol and after allowing the mixture to stand in a refrigerator; total yield 0.41 g, 95%. *Anal.* Calcd for $[Co(C_8H_{22}N_4)(ONO)_2]ClO_4$: C, 22.6; H, 5.2; N, 19.8; Cl, 8.4. Found (fraction 1): C, 22.2; H, 5.1; N, 19.5; Cl, 8.6. Paper chromatography (eluent solution 4:3:2:1 1-butanol–pyridine–water–acetic acid) of such fraction 1 products isolated quickly always showed two bands, the slower moving corresponding to the α-dinitro isomer. Fractions 2 and 3 had visible and pmr spectra intermediate between those of fraction 1 and the α-dinitro complex.

Method C. β-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ (0.10 g) and excess $NaNO_2$ (0.1 g) were allowed to react in ethanol (50 ml) under reflux. The solution became orange-red and then yellow, and after 1 hr the orange solid remaining in suspension was filtered off, washed with ethanol and ether, and dried at 60°; yield 0.06 g containing a little NaCl. The pmr spectrum indicated that this was a mixture containing some α-dinitro isomer. The ethanol solution (containing the sodium salts) was evaporated to dryness, and the pmr spectrum of the yellow solid obtained was identical with that of α-$[Co(4,7\text{-dimetrien})(NO_2)_2]ClO_4$.

The Isomerization β- → α-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ in Methanol. A solution of β-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ in methanol (0.123 g in 30 ml) was refluxed for 3 hr. The visible spectrum of the resulting methanol solution showed a shoulder (660 nm) on the higher wavelength side of band I, typical of α-dichloro isomers, which however was lacking in the visible spectrum of a freshly prepared solu-

(18) H. F. Bauer and W. C. Drinkard, *J. Amer. Chem. Soc.*, **82**, 5031 (1960); *Inorg. Syn.*, **8**, 202 (1966); M. S. Al-Obadie, A. M. Qureshi, and A. G. Sharpe, *J. Inorg. Nucl. Chem.*, **30**, 3357 (1968).

(19) D. J. Francis and G. H. Searle, *Aust. J. Chem.*, in press.

tion of the β complex in methanol. The solution was evaporated to dryness in a current of cold air, and the purple complex was washed with ethanol and ether and dried in a vacuum desiccator; yield 0.107 g (87%). The infrared and visible spectra (maximum ϵ_{559} 151, shoulder at 660 nm) were identical with those of α-[Co(4,7-dimetrien)Cl_2]ClO_4, but the pmr spectra of transformed carbonato complex indicated that about 10% β isomer remained. No green crystals of a trans isomer were evident on microscopic examination of the isomerized dichloro product.

This isomerization also occurred during the transformation of β-[Co(4,7-dimetrien)CO_3]$ClO_4 \cdot H_2O$ to the dichloro complex with hydrogen chloride in methanol. The dichloro product was crystallized in two similar fractions and the infrared and visible spectra indicated that fraction 1 was largely α with some β, and fraction 2 was pure α.

Transformation of α-[Co(4,7-dimetrien)Cl_2]ClO_4 to β-[Co(4,7-dimetrien)CO_3]$ClO_4 \cdot H_2O$. α-[Co(4,7-dimetrien)Cl_2]ClO_4 (0.404 g, 0.001 mol) was treated with Li_2CO_3 (0.4 g) in water (20 ml) over a steam bath. The solution changed from violet to red in a few minutes, and after 1 hr the excess Li_2CO_3 was filtered from the hot solution (pH ~10). The solution was reduced in volume, a little ethanol was added, and the solution was filtered again. $NaClO_4 \cdot H_2O$ (0.14 g) and more ethanol were added, and the solution was left to crystallize in a refrigerator. The fine violet-red needles were filtered off, washed with ethanol and ether, and air-dried; yield 0.371 g, 90%. The pmr spectrum indicated that this crude product was substantially β-[Co(4,7-dimetrien)CO_3]ClO_4 containing about 10% of the α isomer, and this was also demonstrated by passage of a sample of the product through a column of Dowex 50W-X2 cation-exchange resin, Na^+ form, 200–400 mesh, when the two isomers were separated on elution with 0.5 *M* $NaClO_4$ solution.

Isomerization in the Diaquo Complexes. Samples of the α- and β-carbonato perchlorates (~0.095 g) were converted to the respective diaquo complexes by adding 6 *M* $HClO_4$ (0.4 ml) and warming gently. Each solution was diluted with CO_2-free water (10 ml), then partially neutralized to pH 3.00 with carbonate-free NaOH solution, and made up to 35.0 g of solution with 0.0010 *M* $HClO_4$. This gave solutions appropriate for spectrophotometric measurements. The solutions were maintained at 50° in stoppered flasks, and to 7.0-g aliquots, withdrawn at various times, excess $NaHCO_3$ was added to convert the α- and β-diaquo complexes in the mixtures to carbonato complexes. The α- and β-carbonato isomers in each solution were separated chromatographically on a column (65 × 1.8 cm) of Dowex 50W-X2 ion-exchange resin, 200–400 mesh, Na^+ form, by elution with 0.5 *M* $NaClO_4$, and the proportions of the two isomers were determined from atomic absorption analyses (Co) of the eluted bands. Results are given in Table IV.

Results and Discussion

The preparations and reactions of the cobalt(III) complexes of 4,7-dimetrien which have been studied are set out in Figure 3. The α- and β-dichloro, α- and β-carbonato, and α-dinitro perchlorates have been isolated and were isomerically pure. The α- and β-chloroaquo and α- and β-diaquo complexes were generated in solution by treating the dichloro and carbonato perchlorates, of the corresponding α or β geometries, with appropriate solutions of perchloric acid.

Two of the complexes were synthesized, α-dinitro by the conventional aerial oxidation procedure and β-carbonato by substitution of the amine ligand in the tris(carbonato)cobaltate(III) ion. These two synthesized complexes were used to prepare the other complexes by transformation reactions which were expected to occur with full configurational retention on the basis of the retentions observed in the trien complex system.[5,6]

For all these complexes prepared, the α or β geometries were assigned largely from their pmr spectra, although electronic spectra were useful in some instances. Infrared spectra of the complexes run as perchlorate salts or as chloride salts (generally prepared from the perchlorates by ion-exchange conversions), while useful for characterization purposes, were found of no value in assigning or relating the topological configurations.[2,20]

That the α-carbonato perchlorate was isolated from the sequence α-dichloro → α-chloroaquo → α-carbonato and that α-dinitro perchlorate was obtained from α-carbonato → α-diaquo → α-dinitro constitute the main evidence that each of these four transformation steps proceeds with retention of configuration. The first three steps were also followed in solution by pmr which confirmed the full retentions. The corresponding transformations in the β system, β-dichloro → β-chloroaquo → β-carbonato → β-diaquo, were also studied in solution by pmr and each was found to occur with at least a very high degree of configurational retention. These retention reactions are analogous therefore to the observations in the trien system.[5,6]

The isomerization α-dichloro → β-carbonato occurs in alkaline carbonate solution as with α-[Co(trien)Cl_2]$^+$ [6] but the following isomerization reactions have not been observed previously in trien systems: β-dichloro → α-dichloro (in methanol), β-dichloro → α-dinitro ($NaNO_2$ in ethanol), β-chloroaquo → α-chloroaquo (in aqueous acid), β-diaquo → α-dinitro ($NaNO_2$ in aqueous acid). The occurrence of these β → α reactions has enabled the configurations of all these β complexes to be assigned as *RR,SS*-β. The β-dinitro complex could not be obtained. These various reactions and some properties of the new complexes are now discussed in some detail.

Symmetry Properties and Pmr Spectra of the Complexes. Some of the pmr spectra are shown in Figures 4–7, and the assignments of the resonances to $-CH_3$, $-CH_2-$, or NH_2 protons are listed in Table II. These assignments were based on relative peak areas (CH_3:$CH_3{}'$:CH_2:NH_2 = 3:3:12:4) and the characteristic frequency regions for $N-CH_3$ and $-NH_2$ in other cobalt(III) complexes.[21] The sharp methyl resonances in the region 2.3–2.8 ppm downfield from NaTMP are particularly diagnostic of the configurations, but some sharp CH_2 signals were also useful for characterizing a particular complex isomer and for assessing isomeric purity in mixtures.

It is evident from Figure 1 that in the complexes of types α-[Co(4,7-dimetrien)X_2]$^{n+}$ and *RR-trans*-[Co(4,7-dimetrien)-X_2]$^{n+}$ the *N*-methyl substituents are related by the C_2 symmetries. In *RS-trans*-[Co(4,7-dimetrien)X_2]$^{n+}$ the methyl groups are also stereochemically equivalent by the plane of symmetry. The pmr spectra of all complexes of these types would thus be expected to show a single methyl resonance, so that α, *RR-trans*, and *RS-trans* structures may not be distinguishable by this means.

The α-dichloro, -carbonato, -diaquo, and -dinitro compounds all show a single sharp methyl pmr resonance (Table II), but only the α-carbonato complex is unequivocally assigned as α on this basis (Figure 7). The possibilities of trans structures for the three other complexes are excluded on other grounds considered below.

In all the β complexes and also in α-[Co(4,7-dimetrien)-XY]$^{n+}$ the methyl groups are stereochemically nonequivalent (Figure 1), and from the two methyl resonances obtained (3:3) (Table II) the β topologies are assigned to the β-dichloro, -carbonato, and -diaquo compounds. Although the pmr spectra would be expected to be detectably different for the *RR*-β and *RS*-β forms, at least in the methyl resonances,[10] the spectra recorded do not allow an *a priori* assignment of these two isomeric possibilities for the β complexes.

Apart from the methyl resonances, the different symmetries of the α and β structures are also reflected in the NH_2 resonances of the dichloro isomers in DMSO-d_6 (Figure 4). The

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(20) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1563 (1969).

(21) D. A. Buckingham, L. Durham, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 257 (1967).

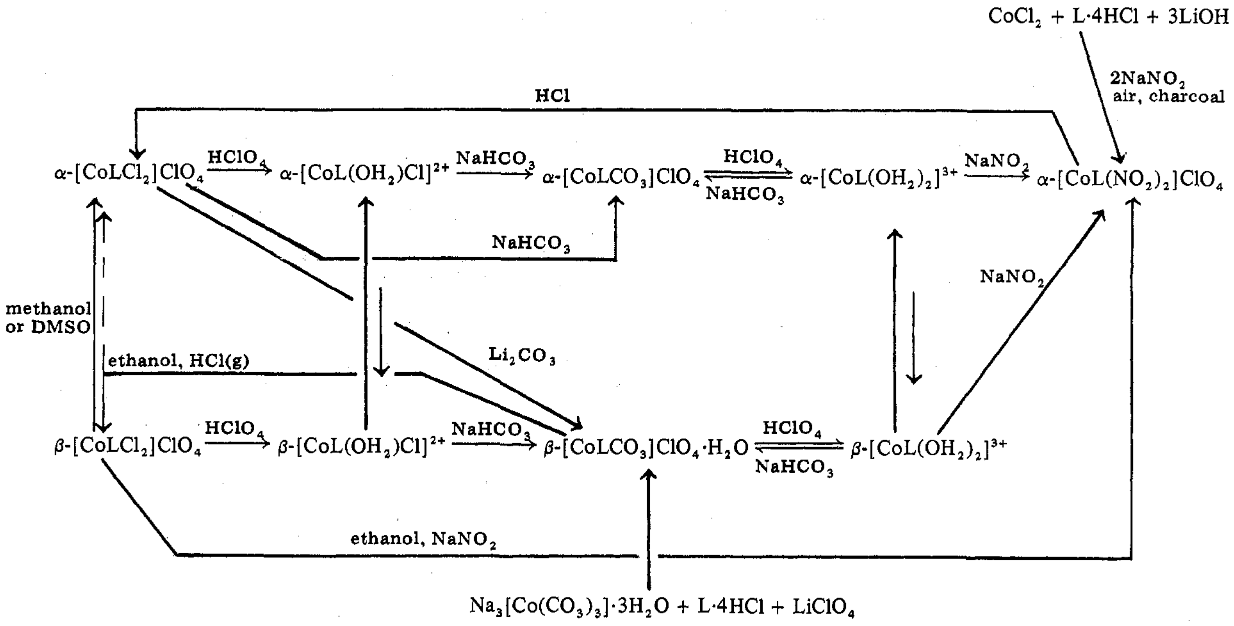

Figure 3. Reaction scheme for syntheses and interconversion reactions of $[CoLX_2]^{n+}$ complexes, L = 4,7-dimetrien.

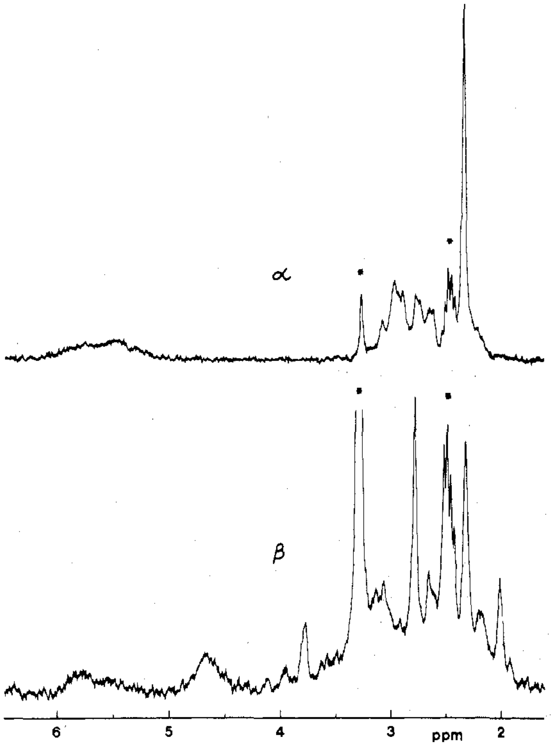

Figure 4. The 60-MHz pmr spectra of α- and β-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ in dimethyl sulfoxide-d_6. Asterisks denote solvent signals.

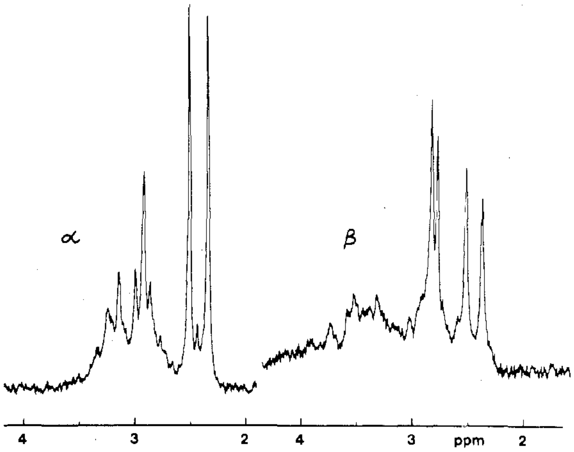

Figure 5. The 60-MHz pmr spectra of α- and β-$[Co(4,7\text{-dimetrien})Cl(OH_2)]^{2+}$ in 10^{-2} *M* D^+ (β run 2 min after dissolving the β-dichloro complex at room temperature).

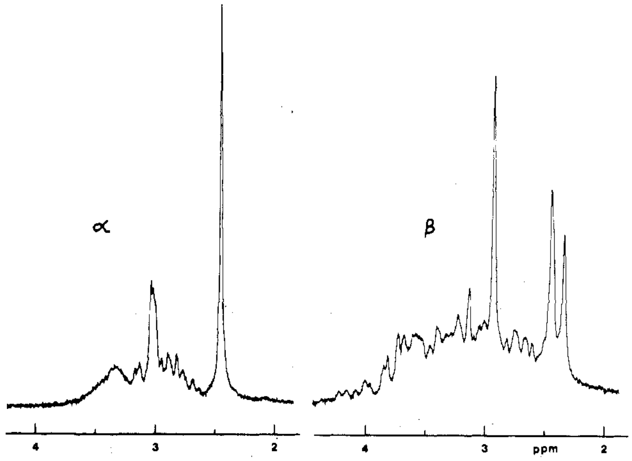

Figure 6. The 100-MHz pmr spectra of α- and β-$[Co(4,7\text{-dimetrien})(OH_2)_2]^{3+}$ in 2 *M* $DClO_4$.

α isomer gives two broad signals (2:2) from the nonequivalent protons within each primary amino group while three broad peaks (1:1:2) are observed from the β isomer.

Assignments of Configuration to the α Complexes. The pmr spectra do not distinguish the α and trans arrangements for the α-dichloro, -diaquo, and -dinitro complexes. However electronic spectra are usually quite different for cis and trans isomers of diacidotetraminecobalt(III) complexes,[22] so that on these two spectral bases *in combination* α configurations can be definitely assigned to these complexes. Table III gives visible spectral data for all the present 4,7-dimetrien complexes, along with the corresponding data for the complexes of the parent trien which offer the most relevant comparisons. In comparing these spectra it is recognized that the absorptions of the 4,7-dimetrien complexes almost in-

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(22) F. Basolo, *J. Amer. Chem. Soc.*, 72, 4393 (1950).

Table II. Chemical Shifts for Pmr Spectra of α- and β-[Co(4,7-dimetrien)X_2]$^{n+}$ Complexes[a]

Complex	Solvent	CH_3	CH_2	NH_2
α-[$CoLCl_2$]$^+$	10^{-2} *M* D^+	2.43	2.6–3.5	~5.7
α-[$CoL(OH_2)Cl$]$^{2+}$	10^{-2} *M* D^+	2.35, 2.52	2.6–3.5, 2.91	~5.7
α-[$CoLCl_2$]$^+$	DMSO-d_6	2.35	2.6–3.1	5.5, 5.7
α-[$CoLCO_3$]$^+$	D_2O	2.68	2.97	
α-[$CoL(OH_2)_2$]$^{3+}$ [b]	2 *M* $DClO_4$	2.44	2.6–3.6, 3.03	5.9, 6.1
α-[$CoL(NO_2)_2$]$^+$	10^{-2} *M* D^+	2.60	2.7–3.2, 2.95, 3.00, 3.13	5.1, 5.6
β-[$CoL(OH_2)Cl$]$^{2+}$	10^{-2} *M* D^+	2.35, 2.50	2.7–3.9, 2.77, 2.82	~5.8
β-[$CoLCl_2$]$^+$	DMSO-d_6	2.32, 2.78	1.9–3.8, 2.02, 3.76	4.7 (mer); 5.5, 5.8 (fac)
β-[$CoLCO_3$]$^+$	D_2O	2.33, 2.45	2.6–3.5, 2.88 (max)	
β-[$CoL(OH_2)_2$]$^{3+}$ [b]	2 *M* $DClO_4$	2.33, 2.43	2.6–4.2, 2.92 (max)	~6.0
β-[$CoL(ONO)_2$]$^+$	D_2O	2.60, 2.70	2.2–3.5, 2.22, 2.90 (max)	

[a] 60-MHz spectra measured in ppm (δ) from sodium trimethylsilylpropanesulfonate for D_2SO_4–D_2O solutions or from tetramethylsilane for dimethyl sulfoxide, as internal references. CH_2 shifts quoted to two decimals are the sharpest or strongest resonances. [b] 100-MHz spectra.

Table III. Electronic Spectral Data[a]

Complex	L = 4, 7-dimetrien				L = trien[b]			
	λ	ε	λ	ε	λ	ε	λ	ε
α-[$CoLCl_2$]ClO_4 [c]	560 660 sh	152	~350 sh		539 600 sh	132	381	135
α-[$CoLCl_2$]ClO_4 [d]	564 660 sh	156	~350 sh					
β-[$CoLCl_2$]ClO_4 [c]					531	131	392	118
β-[$CoLCl_2$]ClO_4 [d]	569	136	~365 sh					
trans-[$CoLCl_2$]ClO_4 [c]					621	53	446	138
α-[$CoL(OH_2)Cl$]$^{2+}$ [c]	540	116	~380 sh		526	118	376	100
β-[$CoL(OH_2)Cl$]$^{2+}$ [c]	547	127	392	112	511	126	376	95
α-[$CoLCO_3$]ClO_4 [f]	515	117	363	118	503	120	357	103
β-[$CoLCO_3$]ClO_4 [f]	525	191	372	171	507	178	358	140
α-[$CoL(OH_2)_2$]$^{3+}$ [e]	515	90	368	66	500	87	359	57
β-[$CoL(OH_2)_2$]$^{3+}$ [e]	516	122	373	108	487	122	357	85
α-[$CoL(NO_2)_2$]ClO_4 [f]	458	238	336	6500	434	212	323	4600
β-[$CoL(NO_2)_2$]ClO_4 [f]					437	241	319	4100
β-[$CoL(ONO)_2$]ClO_4 [f]	478	215	338	3730				

[a] Wavelengths in nm are those of band maxima. [b] Data on the trien complexes are from A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 4, 45 (1965); 6, 787 (1967). [c] Dichloro and chloroaquo spectra measured in 10^{-2} *M* $HClO_4$. [d] Measured in dimethyl sulfoxide. [e] Diaquo spectra measured in 1 *M* $HClO_4$. [f] Carbonato and dinitro spectra measured in water.

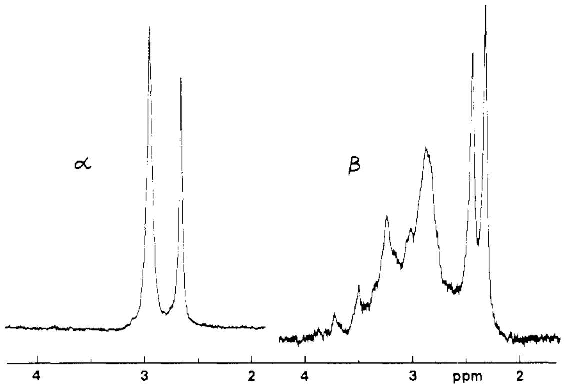

Figure 7. The 60-MHz pmr spectra of α- and β-[Co(4,7-dimetrien)CO_3]ClO_4 in D_2O.

variably occur at higher wavelengths in accordance with the lower ligand field strength of this tertiary amine.

The visible absorption spectrum of purple α-[Co(4,7-dimetrien)Cl_2]$^+$ resembles that of α-[Co(trien)Cl_2]$^+$, not only in the position of the first band maximum allowing for the above ligand field effect but also in the splitting of the $^1A_{1g} \rightarrow {^1T_{1g}}$ (parent O_h) transition which manifests as a shoulder on the high-wavelength side of band I (Table III). This observable splitting of α-dichloro isomers (but not of corresponding β) has been a useful feature to distinguish these α and β geometries in systems of other linear tetramine[12,17,23,24] and dithiadiamine[20,25] ligands. *trans*-Dichlorotetraminecobalt(III) complexes, invariably green, show absorption bands at positions quite different from those of corresponding cis isomers (Table III), and no such green crystals could be identified in the dichloro products obtained in the present work.

For the dinitro complex isolated from the aerial oxidation of cobalt(II) chloride and 4,7-dimetrien·HCl in the presence of sodium nitrite and charcoal, the α arrangement is indicated (rather than the trans) from the similarity in positions of the second visible absorption bands of this complex, the α- and β-dinitro-trien complexes (Table III), and *cis*-dinitro complexes of some substituted trien ligands.[12,24] Band II positions appear to be relatively insensitive to N-methylation (~3 nm to higher wavelengths in the complexes of 1,3,8,10-tetrametrien[1] and 1,11-dimethyl-1,4,8,11-tetraazaundecane compared to the unmethylated situations),[24] although these band II absorptions are usually observed at about 20 nm higher wavelengths in trans than in cis isomers.[22,24] On this basis the trans arrangement may be excluded for the present dinitro-4,7-dimetrien complex.

Further evidence for the α assignment to this dinitro product is its conversion by HCl to the α-dichloro complex,[6] as a *trans*-dinitro complex would not be expected to give only α-dichloro without some evidence of a β product of the intermediate topology.

An α assignment for the α-diaquo complex can be made from the similarity of its visible spectrum to that of α-[Co-

(23) M. Goto, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, 8, 358 (1969).

(24) M. Goto, A. Okubo, T. Sawai, and S. Yoshikawa, *Inorg. Chem.*, 9, 1488 (1970).

(25) B. Bosnich, W. R. Kneen, and A. T. Phillip, *Inorg. Chem.*, 8, 2567 (1969).

(trien)$(OH_2)_2]^{3+}$ (Table III) whereas the spectrum of *RR-trans*-[Co(trien)$(OH_2)_2]^{3+}$ is quite distinct from those of the cis isomers.[7]

Assignments of Configurations to the β Complexes from the Stereochemical Relationships between Isomers. From the pmr spectra the β arrangement has been assigned to the β-dichloro, -carbonato, and -diaquo complexes, and the visible absorption spectra when compared to those of the β-trien compounds (Table III) are consistent with the β structures.

Neither method allows assignment of the conformational forms as *RR,SS*-β or *RS,SR*-β but this can be decided from the stereochemical changes which are possible when these complexes undergo any interconversion or isomerization reactions. Configurational changes at the tertiary nitrogen centers (corresponding to the secondary nitrogens in the parent trien ligand) are precluded by the methyl substituents in the cobalt(III)–4,7-dimetrien complexes unless these centers were to detach from coordination to the metal, and this possibility is considered remote. While all reactions between the 4,7-dimetrien complexes must preserve the *RR* or *RS* nitrogen configurations, topological changes may occur by edge displacements of terminal ethylene bridges (Figure 2). A complex of α topology is constrained to exist in only one conformational form Λ-*RR*-α or Δ-*SS*-α since the $N-CH_3$ bonds at the trigonal nitrogen centers are stereospecifically directed by the bonding of the terminal NH_2 groups in the 1 and 6 positions (Figure 1). Thus the possible stereochemical changes for this system are restricted to Λ-*RR*-α ↔ Δ-*RR*-β ↔ *RR*-trans and Δ-*RS*-β ↔ *RS*-trans. This has the following implications: (1) α complexes can be formed from β complexes only with *RR,SS* configurations; (2) *RS,SR*-β complexes can be formed only in the synthesis reactions or by transformation reactions from other *RS,SR*-β complexes or from meso-trans complexes; (3) the *RR* complexes should be completely inert toward racemization, although Δ-*RS*-β complexes could racemize through the *RS*-trans(meso) structure.

The demonstration of β ↔ α changes as discussed in later sections, involving all the present β complexes (either in transformation or isomerization reactions) thus establishes the *RR,SS*-β configurations for these β complexes.

This preclusion of nitrogen configurational change was expected to allow easier isolation of *RS*-β isomers if these were formed in the synthesis reactions, as these *RS*-β isomers of trien complexes so far studied mutarotate to the more stable[26] *RR*-β in solution.[7,11,15] The products from the synthetic preparations of the α-dinitro and β-carbonato complexes were examined therefore for the presence of *RS*-β isomers.

The pmr spectrum (D_2O) of the total dinitro product isolated from the synthesis as the perchlorate salt (79% yield) showed only a methyl singlet (Table II) with no trace of peaks which might be attributed to the methyl substituents in a β complex topology. The α isomeric purity thus indicated was consistent with only a single yellow dinitro band obtained when this product was chromatographed by various procedures.

Only two sharp methyl signals were shown by the β-carbonato perchlorate isolated from the tris(carbonato)cobaltate(III) preparation, and identical spectra were also obtained when this product was fractionally recrystallized. On this basis the isolated product was isomerically pure, and its conversion to α products (through β-dichloro to α-dichloro or through β-diaquo to α-dinitro, Figure 3) indicates its configuration must be *RR,SS*-β.

Aquation of the Dichloro Isomers. The rate constant for aquation of the α-dichloro to α-chloroaquo complex was determined spectrophotometrically to be $(1.77 \pm 0.05) \times 10^{-4}$ sec^{-1} at 25.0° in $HClO_4$ and showed no variation over the range of conditions studied ($[H^+] = 10^{-2}$-10^{-1} *M*, [Co] = $(2$-$4) \times 10^{-3}$ *M*, $\mu = 10^{-2}$-10^{-1} *M*). This value is closely similar to that for the corresponding α-trien complex[8] ($k = 1.56 \times 10^{-4}$ sec^{-1} at 25°).

Aquation of the β-dichloro isomer to the β-chloroaquo isomer appeared to be complete by the time first measurements of spectra after dissolution in aqueous acid solutions could be taken, so that $t_{1/2}$ is less than 1 min at room temperature giving $k > 1.2 \times 10^{-2}$ sec^{-1}. This aquation rate of the β isomer is considerably faster than the rate for the β-trien analog[8] ($k = 1.43 \times 10^{-3}$ sec^{-1} at 25°). The single pair of methyl resonances in the pmr spectrum in D^+ solution (Figure 5) was consistent with substantially only one β-chloroaquo geometric isomer being generated in the aquation as with the β-trien complex.[8]

That the β-chloroaquo was the species observed immediately on dissolution of β-dichloro in 10^{-2} *M* $HClO_4$ solution was checked in a cell $\mathrm{Ag}\|\mathrm{AgCl}\vdots\mathrm{K_2SO_4}|\mathrm{Hg_2SO_4}\|\mathrm{Hg}$ incorporating an electrode reversible with respect to chloride ion. The emf measured at 1 min, 250 mV, increased by only 5 mV over 2 hr (solution 5×10^{-3} *M* in complex). By comparison, the emf for an equimolar solution of α-[Co(4,7-dimetrien)$Cl_2]ClO_4$ increased from 189 mV (1 min) to a constant value of 254 mV (14 hr), and a rate plot of the data gave $k = 1.2 \times 10^{-4}$ sec^{-1} at 21° which compares well with the spectrophotometric rate.

No satisfactory explanation is available for the difference in reactivities of the two chloro groups for aquation in β-[Co(trien)$Cl_2]^+$,[27] and we are similarly unable to account for the considerable enhancement of reactivity by N-methylation in the β isomer but not in the α. It seems likely however that the greater steric crowding introduced with the methyl substituents is one factor in accelerating the rate of aquation of the β-dichloro complex.[28,29] Reverse trends to these have been shown in acid hydrolysis of the carbonato compounds.[19] The α-carbonato is considerably more reactive than β-carbonato with both trien and 4,7-dimetrien, and N-methylation reduces the reactivity of both the α and β isomers, but other factors may be involved in these reactions.[19]

Formation of chloroaquo complexes was also examined by recording the pmr spectra of the dichloro complexes in 10^{-2} *M* D^+ $(D_2SO_4$-$D_2O)$. The sharp methyl resonance at 2.43 ppm decreased as the α-dichloro complex aquated with the concurrent appearance of the α-chloroaquo methyl signals at 2.35, 2.52 ppm (Figure 5). This process was essentially complete in 2 hr at normal probe temperature, and thereafter little change was observed.

The β-chloroaquo pmr spectrum was measured immediately on dissolving the β-dichloro. Changes in the β-chloroaquo spectrum on standing were small but significant, and by 10

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[26] In β_1-[Co(trien)(gly)]$^{2+}$ the Δ-*RR*-β form is favored over Δ-*RS*-β by <0.1 kcal mol^{-1},[11] but for the other β trien complexes the *RR* form is considerably thermodynamically favored. The stereospecific effects of alkyl substituents on the carbon atoms of the terminal en bridges of the trien ligand may alter the relative stabilities of these isomers considerably so that Δ-*RS*-β can then become favored.[17]

[27] D. A. Buckingham, P. A. Marzilli, I. E. Maxwell, A. M. Sargeson, M. Fehlmann, and H. C. Freeman, *Chem. Commun.*, 488 (1968).

[28] D. A. Buckingham, B. M. Foxman, and A. M. Sargeson, *Inorg. Chem.*, 9, 1790 (1970).

[29] D. A. Buckingham, M. Dwyer, A. M. Sargeson, and K. J. Watson, *Acta Chem. Scand.*, 26, 2813 (1972), and private communication.

min small new peaks which were identified with α-chloroaquo CH_2 resonances had appeared. Subsequent changes were slow but at no stage could β- or α-diaquo peaks be recognized in the spectrum. Further evidence for significant β- → α-chloroaquo isomerization was adduced by transforming β-chloroaquo solutions to carbonato complexes as discussed in a later section.

Retention Reactions in the α System. α-Dichloro → α-Chloroaquo → α-Carbonato. The conversion on a preparative scale of α-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ through the α-chloroaquo to the pure α-carbonato complex with $NaHCO_3$ proves the isomeric purity of the dichloro complex and demonstrates the full retention of configuration in these two steps. If the aquation step is prolonged, some β-carbonato product can arise in this preparative procedure,[19] and the conditions necessary to form the α-carbonato isomer with the complete exclusion of the β isomer were established from a series of small-scale reactions, with the α- and β-carbonato isomers being separated by ion-exchange chromatography. For aquation times up to 2 hr in 10^{-2} *M* $HClO_4$ at 50° and complex concentration 10^{-2} *M*, the α-carbonato product was obtained exclusively after adding $NaHCO_3$. Even when the dichloro complex was dissolved in acid quickly at room temperature and treated with $NaHCO_3$ immediately, no β band was evident in the subsequent chromatography. This implies that hydrolysis of the dichloro complex in the weakly basic $NaHCO_3$ solution (pH ~8) also occurs with retention of configuration.[30] At 3-hr aquation time (50°) the carbonato-dimetrien product contained a trace of β isomer, and the proportion of final β-carbonato complex increased with longer aquation times and was substantial (~25% β) at 6 days of aquation.

These two steps were also studied by pmr. Samples of α-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ were dissolved in 10^{-2} *M* D^+-D_2O in pmr tubes and excess $NaHCO_3$ was added to the different tubes after various times. When $NaHCO_3$ was added immediately (dichloro) or when aquation to the α-chloroaquo complex was complete (2.5 hr at 40°), the resulting α-carbonato spectra showed only a trace (<4%) of β-carbonato isomer. After prolonged aquation (2.5 days at 40°) treatment with $NaHCO_3$ gave carbonato product containing about 20% of β isomer. Separate experiments established that the extent of isomerization of the α-diaquo complex is almost negligible under these conditions, so that the β isomer must arise here through some isomerization α- → β-chloroaquo.

α-Carbonato → α-Diaquo → α-Dinitro. The preparative conversion of the α-carbonato through the α-diaquo to give the α-dinitro perchlorate in high yield indicates that these steps each proceed with essentially complete retention of configuration.[5,31]

α-Diaquo → α-Carbonato. This retention was studied by pmr. α-Carbonato perchlorate was dissolved in 2 *M* D^+-D_2O in a pmr tube and the α-diaquo spectrum was recorded. Addition of excess $NaHCO_3$ regenerated the α-carbonato complex and a trace only of the β isomer was evident from the spectrum then recorded.

Retention Reactions in the β System. Reactions β-dichloro through β-chloroaquo and β-carbonato to β-diaquo were examined in solution using pmr as described for the α system. Excess $NaHCO_3$ was added to samples of β-dichloro perchlorate in 10^{-2} *M* D^+-D_2O (≡β-chloroaquo) in different pmr tubes. When bicarbonate was added immediately after dissolution of the sample in the acid, the resulting β-carbonato spectrum showed only a small proportion of the α-carbonato isomer (~3%). Bicarbonate addition to the β-chloroaquo complex after standing gave increasing proportions of the α-carbonato complex with longer times (~10% after 30 min, ~30% after 1.5 days at 35°).

These experiments demonstrate that the β-chloroaquo → β-carbonato transformation proceeds with configurational retention (⩾97%) as in the α case, and this provides a sensitive method for assessing the isomeric purity of any dichloro sample. Addition of excess $NaHCO_3$ immediately after dissolution in D^+ solution gives the carbonato complex, with full retention from each isomer, and the sharp α and β methyl resonances are well separated in the (mixed) pmr spectrum (Figure 7).

The significant amount of α-carbonato complex obtained after the β-chloroaquo complex had stood for 30 min is attributed to β- → α-chloroaquo isomerization, as α-chloroaquo peaks (but not β- or α-diaquo) were recognized in the pmr spectrum of a β-chloroaquo solution within this time. Significant involvement of diaquo species in the isomerization would have required the amount of aquation β-chloroaquo → β-diaquo to be substantial within 30 min and this should have been apparent in the emf experiment discussed earlier.

The sequence

$$\beta\text{-carbonato} \xrightarrow{2\,M\ D^+} \beta\text{-diaquo} \xrightarrow{NaHCO_3} \beta\text{-carbonato}$$

was followed by pmr as for the α system. About 10% isomerization to α had occurred on regeneration of the carbonato, and this isomerization in the diaquo complexes is discussed below.

Isomerization Reactions. (a) α-Dichloro → β-Carbonato. Reaction of the α-dichloro complex with Li_2CO_3 in water gave predominantly the β-carbonato complex in the isolated product, as in the trien system.[6] This isomerization α → β (Figure 2) probably occurs in an initial base hydrolysis to the chlorohydroxo complex, which is succeeded by substitution of bicarbonate ion with retention of the β configuration,[30] so that no inference can be made as to the relative carbonato isomer stabilities. For similar reasons we feel that the isolation of the β-carbonato isomer exclusively from the tris(carbonato)cobalt(III) reaction does not necessarily indicate that the β-carbonato isomer is thermodynamically favored over α.

(b) β-Diaquo → α-Diaquo. In the trien system a greater stability for a β configuration over α was demonstrated only for the diaquo complexes,[6,13] so that the α- ⇌ β-diaquo equilibrium in the present system was of some interest. However the present diaquo experiments could not be brought to a quantitative conclusion as the isomerization starting from the β complex was not a clean reaction and generated some cobalt(II), so that equilibrium was not established between the two diaquo isomers under any of the conditions used (pH 2, 3, or 6; temperature 40, 50, or 70°) within some days.

In one experiment separate solutions of the α- and β-diaquo complexes in $HClO_4$-$NaClO_4$, adjusted to pH 3.0, were allowed to isomerize at 50° and the reactions were examined by two methods. The spectrophotometric changes (band maxima are listed in Table IV) were consistent with the β form initially isomerizing to the α isomer (solution composition calculated about 30% α and 70% β after 6 hr). The spectrum of the α solution indicated the degree of isomerization of α → β as only 6% after 60 hr.

A less direct method of studying these reactions involved

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[30] About 20% inversion for the reaction of *cis*-$[Co(en)_2Cl_2]^+$ with $NaHCO_3$ is reported by F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Amer. Chem. Soc.*, **85**, 1215 (1963).

[31] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 230-231, 291-294.

Table IV. Isomerization of α- and β-[Co(4,7-dimetrien)$(OH_2)_2$]$^{3+}$ at 50°, pH 3.0, and [Co] = 0.007 *M*

	Starting soln α-diaquo			Starting soln β-diaquo					
Time, hr	pH	ϵ_{515}	ϵ_{368}	pH	λ	ε	λ	ε	% α from chromatography of carbonato isomers
0	3.00	91.4	68.4	3.00	516	124.4	373	108	23
6	2.97	91.5	68.7	2.95	516	114.5	371	98	
20		92.0	69.4		515	113.0	368	108	55
40		92.5	70.1		514	110.3	362	128	
60	2.95	93.2	71.0	2.81	511	105.8	~350 sh	~161	67

transforming the mixed α- and β-diaquo complexes in aliquots of the above solutions to the α- and β-carbonato complexes which were separated chromatographically and the proportions were assessed. This method requires that the conversion of each diaquo isomer to the corresponding carbonato isomer with bicarbonate be rapid compared to the isomerization at pH 8 (bicarbonate solution) so that the transformation occurs with retention of configuration.[5,13] This condition is essentially achieved with the present α-diaquo → α-carbonato conversion (from the pmr experiment discussed above) so that a zero-time sample of α-diaquo solution when transformed and chromatographed gave 98% recovery of α, and a β band was not detectable. The β-diaquo → β-carbonato transformation does not take place with full retention however (pmr experiment; Table IV zero-time sample chromatographed gave 23% α and 77% β, with 99% cobalt recovery from these two carbonato bands) and the isomerization probably occurs through the β-hydroxoaquo complex in the pH 8 conditions involved. The trend in the chromatography figures (Table IV) does indicate however that substantial isomerization takes place in the β-diaquo solution.

It is clear from both the above methods that while the α-diaquo complex undergoes little isomerization, the β-diaquo complex generates substantial α-diaquo isomer under similar conditions, and from these relative rates we deduce that the α-diaquo isomer is considerably favored thermodynamically.

(c) **β-Diaquo → α-Dinitro.** Substitutions of nitrite ion in the α- and β-[Co(trien)$(H_2O)_2$]$^{3+}$ isomers[5,6] and in α-[Co(4,7-dimetrien)$(OH_2)_2$]$^{3+}$ produce (after standing) the corresponding dinitro complexes with retentions of configurations. However it proved impossible to prepare the β-[Co(4,7-dimetrien)$(NO_2)_2$]$^+$ complex by this procedure from the corresponding β-diaquo complex; the final product obtained (method A, Experimental Section) was always yellow α-[Co(4,7-dimetrien)$(NO_2)_2$]ClO_4, as established from comparisons of the pmr and infrared spectra and X-ray powder pattern with those of the α compound obtained from the aerial oxidation synthesis.

A red-orange complex was obtained however when conditions were arranged that the product crystallized from solution rapidly after addition of the nitrite (method B, fraction 1). Ion-exchange chromatography established the complex to be a 1+ ion, and the analysis and visible spectrum (Table III) indicated that it was (or at least contained) an intermediate nitrito complex. Stronger infrared absorption over 1000-1050 cm^{-1} (although on the side of the perchlorate band) than in all other "β" and α samples was consistent with a nitrito complex,[31] although the 820-cm^{-1}-NO_2 deformation band was also present. From its rapid formation[31] we propose that the β configuration was retained at this stage, and we accordingly assign this red complex as (largely) β-[Co(4,7-dimetrien)$(ONO)_2$]ClO_4. We assign the two sharpest and strongest pmr peaks (Table II), which appear to be of unequal intensities, to N-CH_3 resonances (δ 2.60, 2.70 ppm), and one of these coincides with that from the α-dinitro complex (δ 2.60 ppm). The spectrum is thus consistent with a product mixture, and paper chromatography gave two bands with one corresponding to the α-dinitro complex. Other components could be any of the possible nitritonitro isomers (Figure 8). This red intermediate complex rearranged in D_2O, and after 8 hr at 50° the pmr spectrum had become identical with that of the α-dinitro complex.

(d) **β-Dichloro → α-Dinitro.** In an attempt to avoid this β → α isomerization, β-[Co(4,7-dimetrien)Cl_2]ClO_4 was treated with nitrite in ethanol (method C). The resulting ethanol solution contained only the α-dinitro complex (identified by pmr spectrum), and the orange material remaining suspended was apparently a mixture of nitrito complexes. The pmr changed slowly with time to become identical with that of the α-dinitro complex.

Nitrito → nitro isomerizations usually occur intramolecularly with retention of the configuration about the metal center,[31] but in the present instance it seems that there is simultaneous movement of the terminal "planar" chelate ring to give the α complex topology. Competing reaction paths are then possible, with the formation of three isomeric nitritonitro complexes (Figure 8), two of which could subsequently convert directly to the α-dinitro complex. Such a scheme would then account for the varying pmr spectra observed from the different "β" samples isolated and during their subsequent rearrangement on standing in D_2O. The strong methyl resonance at 2.60 ppm was present at all stages however.

Whatever the mechanism, the fact that the β → α isomerization occurs to completion indicates that the methyl substituents exercise considerable effect in destabilizing the β complex configuration relative to the α in the dinitro complexes, and this is consistent with no β isomer being detected in the dinitro aerial oxidation synthesis in the presence of charcoal.

(e) **β- → α-Chloroaquo.** Evidence was given earlier for isomerization occurring in solutions of both the α- and β-chloroaquo isomers. From the extents of isomerization determined (β gives 30% α after 1.5 days at 35°; α gives 20% β after 2.5 days at 40°) it is clear that the β- $\rightleftharpoons$ α-chloroaquo equilibrium favors the α isomer. Isomerizations of *cis*-chloroaquo complexes were not observed in the trien system,[8,32] although *cis*-[Co(en)$_2$Cl(OH_2)]$^{2+}$ isomerizes to the trans isomer.[33]

(f) **β-Dichloro → α-Dichloro.** The isomerization β- → α-[Co(4,7-dimetrien)Cl_2]ClO_4 in methanol is a striking difference from the trien system. Methanol frequently induces isomerization in dichlorotetraminecobalt(III) complexes, but these are usually cis → trans with bis(ethylenediamine) type

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[32] G. H. Searle and A. M. Sargeson, *Aust. J. Chem.*, 26, 661 (1973).

[33] A. M. Sargeson, *Aust. J. Chem.*, 16, 352 (1963).

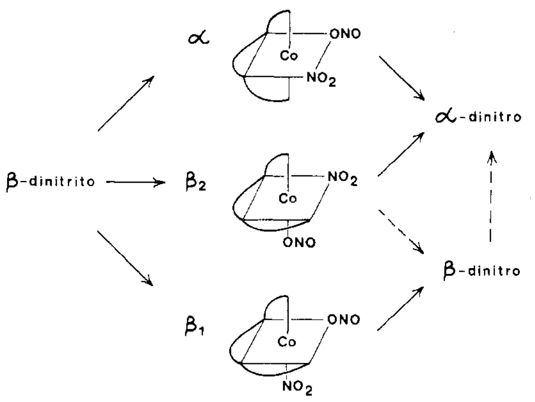

Figure 8. Possible reaction routes for nitrito-nitro isomerization and $\beta \rightarrow \alpha$ isomerization.

complexes[34] or $\beta \rightarrow$ trans with trien[6] and some carbon-methylated trien ligands.[12,23] The different solvation properties of methanol compared to water have seemed therefore to favor *trans*-dichloro configurations. With the present $[Co(4,7\text{-dimetrien})Cl_2]^+$ system, we take the observed $\beta \rightarrow \alpha$ isomerization to indicate a considerably reduced stability of the trans configuration.

This isomerization β- $\rightarrow$ α-$[Co(4,7\text{-dimetrien})Cl_2]ClO_4$ also occurred in dimethyl sulfoxide. The pmr spectra of the two dichloro isomers in dimethyl sulfoxide-d_6 (Figure 4) had become identical after equilibration (14 hr at 50°), and this equilibrium spectrum clearly represented an α configuration (mainly α-dichloro with a little solvent-substituted product) since the signal from the meridional NH_2 (4.7 ppm) in the β configuration was absent. Similarly the α-dichloro visible spectrum in this medium (Table III) was exactly reproducible after 20 hr at room temperature, but the spectrum of the β-dichloro complex changed slowly over several hours due largely to solvolysis.

Relative Stabilities of the α and β Isomers. Studies on the parent trien complexes showed that the relative thermodynamic stabilities of the α, β, and trans configurations depend on the substituents X and on the solvent used (water or methanol).[6] For the same acido substituents X there is a considerable dependence of these relative geometric isomer stabilities on the alkyl substitution in the tetramine chain, although the previous investigations with complexes of C- and (terminal N)-methylated trien ligands have not always allowed firm statements in this regard. Some of the dichloro and dinitro complexes which have been isolated from aqueous solutions might not be the most stable isomers (sometimes yields were low or not reported) and this is especially so if charcoal has not been present to ensure equilibration; some preparations or isolations have involved alcoholic media in which isomerizations can occur. It seems clear from aerial oxidation syntheses of dichloro and/or dinitro complexes (compared with the results of similar syntheses of the trien complexes) that the stability of the *RR,SS*-trans configuration is enhanced with the ligands 1,10-dimetrien,[24] 1,5,10-trimetrien,[24] and active 3,8-dimetrien,[17] and that the stability of the *RR,SS*-β form over the α form is enhanced with the ligands 5-metrien,[23] active 5,6-dimetrien,[23] and *meso*-3,8-dimetrien.[12] Moreover *RS,SR*-β isomers (rather than *RR,SS*-β) were obtained with the ligands active 2,9-dimetrien,[17] *2S,5R,9S*-trimetrien,[35] and active 3,8-dimetrien.[17] These stabilizations have generally been rationalized on the basis of minimization of nonbonded atomic interactions (which is the basis of the accepted requirement that substituent methyls be equatorially disposed with respect to the chelate ring plane).[17,23,24,35]

The foregoing results for the 4,7-dimetrien complexes indicate that the α topology is thermodynamically favored over the β (and trans) in the dichloro (in methanol), chloroaquo, diaquo, and dinitro complexes. Moreover the stability of the α arrangement has become enhanced from that in the corresponding trien complexes with dichloro (where $\beta \rightarrow$ trans in methanol),[6] diaquo (where $\alpha/\beta = 0.30$ at equilibrium)[13] and dinitro (where $\alpha/\beta \approx 3$).[6] Dreiding models of the present complexes indicate that the magnitudes of the most serious nonbonded interactions, those between the methyl substituents and either the acido substituents X or the primary amine groups, are likely to be in the order $\alpha \ll RR\text{-}\beta \sim RS\text{-}\beta < RR\text{-}$trans $\sim RS$-trans. The observed relative isomer stabilities may also be rationalized on the basis that the larger *N*-methyl substituents induce greater bond angle strains at the tertiary nitrogen donor centers compared with the trien situation, so that the normal trigonal or "angular" bonding situation becomes even more preferred. While the angle strain at one "planar" nitrogen center can clearly be accommodated in the β complexes here reported, we doubt whether trans complexes of this ligand will be possible.

The effect of (secondary *N*)-methylation in favoring trigonal coordination at that nitrogen donor position is also apparent from studies on the topological isomers of $[Co(\text{trenen})Cl]^{2+}$ (trenen = 4-(2-aminoethyl)-1,4,7,10-tetraazadecane) and $[Co(7\text{-metrenen})Cl]^{2+}$.[29] Energy minimization calculations indicate that nonbonded atomic interactions of the type mentioned account for the observed relative isomer stabilities in these trenen systems.

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Registry No. α-$[CoLCl_2]ClO_4$, 42885-93-8; β-$[CoLCl_2]ClO_4$, 42949-46-2; α-$[CoLCl_2]Cl\cdot 2H_2O$, 42885-94-9; β-$[CoLCl_2]Cl\cdot H_2O$, 42885-95-0; α-$[CoLCO_3]ClO_4$, 42885-96-1; β-$[CoLCO_3]ClO_4\cdot H_2O$, 42885-97-2; α-$[CoLCO_3]Cl$, 42949-47-3; β-$[CoLCO_3]Cl\cdot 2H_2O$, 42885-98-3; α-$[CoL(NO_2)_2]ClO_4$, 42885-99-4; α-$[CoL(NO_2)_2]Cl\cdot 0.5H_2O$, 42942-72-3; α-$[CoL(OH_2)Cl]^{2+}$, 42893-10-7; β-$[CoL(OH_2)Cl]^{2+}$, 42893-11-8; α-$[CoL(OH_2)_2]^{3+}$, 42893-12-9; β-$[CoL(OH_2)_2]^{3+}$, 42893-13-0; β-$[CoL(ONO)_2]ClO_4$, 42942-74-5; $Na_3[Co(CO_3)_3]\cdot 3H_2O$, 15684-40-9.

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[35] M. Saburi, T. Sawai, and S. Yoshikawa, *Bull. Chem. Soc. Jap.*, **45**, 1086 (1972).